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Description

The invention relates to a process for preparing a silver catalyst, suitable for use in the oxidation of ethylene to ethylene oxide, to the silver catalyst so prepared and to a process for preparing ethylene oxide.

It is generally known that silver catalysts are applied in the oxidation of ethylene to ethylene oxide. It is referred to the Netherlands patent application 7300162, in which a silver catalyst is disclosed. Moreover there is disclosed the application of small amounts of one or more promoters, such as cesium compounds, rubidium compounds and potassium compounds. In the process of EP-A-172 565, a sodium component is deposited onto an alpha-alumina carrier and the impregnated carrier steam heated prior to the deposition of the silver compound and the Ba, Cs - promoters.

It has been observed that the above-mentioned silver catalysts during use become less stable, which means that the selectivity and the activity of the catalysts become lower and generally it is more economical to replace them by new silver catalysts after some years.

It is the object of the invention to find silver catalysts with improved stability.

Applicant has now found silver catalysts with improved stability. The impregnation of a support with silver and promoting metals is also disclosed in the applicant's earlier application EP-A- 266 015.

This invention relates to a process for preparing a silver catalyst, suitable for use in the oxidation of ethylene to ethylene oxide comprising impregnating an alumina carrier with a solution of a silver compound, sufficient to cause precipitation on the carrier of from 1 to 25 per cent by weight, on the total catalyst, of silver, and after precipitation, reducing the silver compound to metallic silver, characterized in that the alumina carrier is mixed with an alkali metal compound and calcined to a temperature of between 1200 °C and 1700 °C prior to impregnation with the solution of the silver compound and before, during or after that impregnation the calcined carrier is also impregnated with one or more dissolved potassium, rubidium or cesium compounds as promoter and with a rhenium compound as co-promoter.

If desired a sulphur compound is impregnated on the carrier.

The carrier used in the inventive process for the preparation of silver catalysts, is an alkali metal enriched alumina carrier, which has been calcined, to a temperature of between 1200 °C and 1700 °C. A large part of the calcined material will be alpha-alumina, but the existence of spinels or other configurations can not be excluded, since the calcined material is enriched with alkali metal. Salts or

hydroxide of an alkali metal have been mixed with the original alumina. Suitable salts include fluorides, nitrates, chlorides and sulphates. Suitable metals are lithium, sodium, potassium, rubidium and cesium. Preferred compounds are cesium fluoride, cesium chloride, lithium fluoride, lithium nitrate and cesium hydroxide. Preferably the alkali metal compound is mixed with the alumina in such quantity that the atomic ratio of alkali/aluminium is between 0.001 and 0.1. If desired silicon dioxide is additionally mixed with the alumina in such quantity that the atomic ratio of silicon/aluminium is between 0.1 and 0.5. The aluminas may be modifications which by calcination provide alpha-alumina, such like gamma-alumina. Hydrated aluminas may also be suitable, such as boehmite, which latter by calcining via gamma-alumina provides alpha-alumina.

Preferably the carrier is prepared by mixing the alumina with water and an alkali metal salt or hydroxide, extruding the obtained mixture to shaped particles and calcining the shaped particles, preferably to a temperature between 1200 °C and 1700 °C. The calcination may be carried out in one or more steps, depending on the choice of alumina modification. Generally a sufficient amount of water is added to form a paste suitable for extrusion. The obtained extrudable paste is then extruded and shaped to particles. The shaped particles are heated in order to evaporate the water. The solid particles are then calcined, preferably to a temperature between 1200 °C and 1700 °C.

Suitable aluminas are powders of gamma-alumina, alpha-alumina monohydrate, alpha-alumina trihydrate or beta-alumina monohydrate, which powder during calcination are sintered. At the calcination temperature the crystal structure may be modified. The cubic structure of gamma-alumina is converted into the hexagonal structure of alpha-alumina, depending on the amount and nature of the additive used. The catalytically active surface of the enriched alumina may be between 0.1 and 5 m²/g, preferably between 0.2 and 2 m²/g. The shaped alumina particles comprise i.a. bars, rings, pellets, tablets and triangles. They are especially suitable in fixed bed applications in ethylene oxide preparation.

In order to prepare a suitable catalyst the calcined, alkali metal enriched alumina carrier is impregnated with a solution of a silver compound sufficient to cause precipitation on the carrier of from 1 to 25 per cent by weight, on the total catalyst, of silver, the so impregnated carrier is separated from the solution and the precipitated silver compound is reduced to metallic silver. Hereinafter several detailed methods will be disclosed.

As a promoter is added to the silver solution,

one or more of the alkali metals potassium, rubidium and cesium, preferably in the form of their salts or hydroxides. Although the metals potassium, rubidium and cesium in pure metallic form exist, they are in that form not suitable for use. Therefore they are administered in a solution of their salts or hydroxide. The alumina carrier is impregnated with the promoter before, during or after the impregnation of the silver salt has taken place. The promoter may even be brought on the carrier after reduction to metallic silver has taken place. The amount of promoter generally lies between 10 and 1000 parts by weight of potassium, rubidium or cesium metal per million parts by weight of total catalyst. Preferably amounts between 250 and 750 parts by weight are present on the total catalyst.

The alumina carrier is also impregnated with a rhenium compound. This may be done the same time that the promoter is added, before or later. The amount of rhenium, calculated as the metal, brought on the alumina carrier is between 100 and 2000 parts by weight per million parts by weight of total catalyst.

Preferably the rhenium compounds used in the preparation of the catalyst according to the invention are rhenium salts, a rhenium oxide or a rhenium sulphide.

As rhenium salts may be mentioned rhenium halides, such as rhenium tetrafluoride, rhenium hexafluoride, rhenium trichloride, rhenium pentachloride, rhenium tribromide, rhenates and perrhenates.

As oxides of rhenium may be mentioned rhenium sesquioxide (Re_2O_3), rhenium dioxide (ReO_2), rhenium trioxide (ReO_3) and rhenium heptoxide (Re_2O_7). Of the perrhenates used in the process according to the invention especially ammonium perrhenate is suitable.

As already mentioned hereinbefore with the rhenium compound also a sulphur compound may be used. It is preferred to use a combination of said compounds. The sulphur compound is preferably added in the form of ammonium sulphate, but other sulphur compounds may be used as well, such as sulphonates, thiols, dimethyl sulfoxide, sulphates, sulphites or thiosulphates.

The rhenium compound (calculated as the metal) in the catalyst is preferably used in an amount of between 100 and 2000 parts by weight per million parts by weight of total catalyst. The sulphur is preferably used in equimolar amounts with respect to the rhenium, but somewhat higher and somewhat lower amounts of sulphur are not excluded.

Preferably as a sulphur compound a sulphate is applied, more preferred ammonium sulphate is applied.

It has been found that sulphate ions are

present on the carrier in an amount between 20 and 500 parts by weight per million parts by weight of total catalyst.

Generally the alumina carrier is mixed with a silver salt or a silver salt-complex containing aqueous solution, so that the alumina carrier is impregnated with said aqueous solution, thereafter the impregnated carrier is separated from the aqueous solution, e.g. by filtration and then dried. The thus obtained impregnated alumina carrier is heated to a temperature in the range of from 100 °C to 400 °C, during a period sufficient to cause reduction of the silver salt (complex) to metallic silver and to form a layer of finely divided silver, which is bound to the surface of the alumina carrier. A reducing gas or an inert gas may be conducted over the alumina carrier during this heating step.

There are known several methods to add the silver to the alumina carrier. The carrier may be impregnated with an aqueous silver nitrate containing solution, and then dried after which drying step the silver nitrate is reduced with hydrogen or hydrazine. The alumina carrier may also be impregnated with an ammoniacal solution of silver oxalate or silver carbonate, and then dried, after which drying step the silver oxalate or silver carbonate is reduced to metallic silver by heating to e.g. up to 400 °C. Specific solutions of silver salts with solubilizing and reducing agents may be employed as well, e.g. combinations of vicinal alkanolamines, alkyldiamines and ammonia.

The amount of promoter generally lies between 10 and 1000 ppm of alkali metal calculated on the total carrier material. Preferably amounts between 250 and 750 ppm are especially suitable. Suitable compounds of potassium, rubidium and cesium are, for example, the nitrates, oxalates, carboxylic acid salts or hydroxides. The most preferred promoter is cesium among the alkali metals, preferably applied in an aqueous solution of cesium hydroxide or cesium nitrate.

There are known excellent methods of applying the promoters coincidentally with the silver on the carrier. Suitable alkali metal salts are generally those which are soluble in the silver-precipitating liquid phase. Besides the above-mentioned compounds may be mentioned the nitrites, chlorides, iodides, bromides, bicarbonates, acetates, tartrates, lactates and isopropoxides. The use of alkali metal salts which react with the silver salt in solution must be avoided, e.g. the use of potassium chloride together with silver nitrate in an aqueous solution, since then silver chloride is prematurely precipitated. The use of potassium nitrate is recommended instead of potassium chloride. However potassium chloride may be used together with a silversalt-amine-complex in aqueous solution, since then silver chloride is not precipitated prematurely

from the solution.

The amount of promoter on the alumina carrier may also be regulated within certain limits by washing out the surplus of alkali material with methanol or ethanol. Temperatures, contact times and drying with gases may be regulated. Traces of alcohol in the pores of the carrier must be avoided.

A preferred process of impregnating the alumina carrier consists of impregnating the carrier with an aqueous solution containing a silver salt of a carboxylic acid, an organic amine, a salt of potassium, rubidium or cesium. A potassium containing silver oxalate solution may be prepared. Silver oxide (slurry in water) is reacted with a mixture of ethylene diamine and oxalic acid, so that an aqueous solution of silver oxalate-ethylene diamine-complex is obtained, to which solution is added a certain amount of potassium compound. Other amines, such as ethanolamine, may be added as well. A potassium containing silver oxalate solution may also be prepared by precipitating silver oxalate from a solution of potassium oxalate and silver nitrate and rinsing with water or alcohol the obtained silver oxalate in order to remove the adhering potassium salt until the desired potassium content is obtained. The potassium containing silver oxalate is then solubilized with ammonia and/or an amine in water. Rubidium and cesium containing solution may be prepared also in these ways. The impregnated alumina carriers are then heated to a temperature between 100 °C and 400 °C, preferably between 125 °C and 325 °C.

It is observed that independent of the form in which the silver is present in the solution before precipitation on the carrier, the term "reduction to metallic silver" is used, while in the meantime often decomposition by heating occurs. We prefer to use the term "reduction", since the positively charged Ag^+ ion is converted into metallic Ag atom. Reduction times may generally vary from 5 min to 8 hours, depending on the circumstances.

The promoter on the alumina surface is preferably present in the form of oxide potassium, rubidium or cesium. Mixtures of oxides are not excluded.

The silver catalysts according to the present invention have been shown to be particularly selective and stable catalysts in the direct oxidation of ethylene with molecular oxygen to ethylene oxide. The conditions for carrying out such an oxidation reaction in the presence of the silver catalysts according to the present invention broadly comprise those already described in the prior art. This applies, for example, to suitable temperatures, pressures, residence times, diluent materials, such as nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, presence or absence of moderating agents to control the catalytic

action, for example, 1-2-dichloroethane, vinyl chloride or chlorinated polyphenyl compounds, the desirability of employing recycle operations or applying successive conversions in different reactors to increase the yields of ethylene oxide, and any other special conditions which may be selected in processes for preparing ethylene oxide. Pressures in the range of from atmospheric to 35 bar are generally employed. Higher pressures are, however, by no means excluded. Molecular oxygen employed as reactant can be obtained from conventional sources. The suitable oxygen charge may consist essentially of relatively pure oxygen, a concentrated oxygen stream comprising oxygen in major amount with lesser amounts of one or more diluents, such as nitrogen and argon, or another oxygen-containing stream, such as air. It is therefore evident that the use of the present silver catalysts in ethylene oxidation reactions is in no way limited to the use of specific conditions among those which are known to be effective.

In a preferred application of the silver catalysts according to the present invention, ethylene oxide is produced when an oxygen-containing gas is contacted with ethylene in the presence of the present catalysts at a temperature in the range of from 190 °C to 285 °C and preferably 200 °C to 270 °C.

Generally in the reaction of ethylene with oxygen to ethylene oxide, the ethylene present is at least a double amount (on a mol basis) compared with the oxygen, but the applied amount of ethylene is often much higher. Therefore the conversion is calculated according to the mol percentage of oxygen, which has been used. The oxygen conversion is dependent on the reaction temperature, which latter is a measure for the activity of the catalyst employed. The values T_{30} , T_{40} and T_{50} indicate the temperatures at 30 mol%, 40 mol% and 50 mol% conversion of the oxygen respectively in the reactor, and the values T are expressed in °C. These temperatures are higher when the conversion of the oxygen is higher. Moreover these temperatures are strongly dependent on the employed catalyst and reaction conditions. The selectivities (to ethylene oxide) indicate the molar percentage of ethylene oxide in the reaction mixture compared with the total molar amount of converted matter. The selectivity is indicated e.g. as S_{30} , S_{40} and S_{50} , which means the selectivity at 30, 40 and 50 mol% oxygen conversion respectively.

The stability of the silver catalyst cannot be expressed directly. To measure the stability experiments during a considerable time, e.g. a year would be necessary. Applicant has now found that these time consuming tests can be simulated by carrying out the experiments during about one month under the extreme high velocity of thirty

thousand litres gas.litre catalyst⁻¹.h⁻¹(also indicated as GHSV). This velocity is much higher than that used in commercial ethylene oxide processes (the latter GHSV = 3300). During the whole test period the above defined S and T values are measured regularly. After the reaction has finished, the total amount of produced ethylene oxide per ml of catalyst is determined. The selectivity and the activity of the catalyst are extrapolated on the basis that one ml of catalyst would have produced 1000 g of ethylene oxide. The new catalyst is considered to be more stable than a standard catalyst, if the differences in T- and S-values, measured on the new catalyst (preferably at the beginning and at the end of the reaction) are smaller than those measured on the standard catalyst, which in every experiment is present. The stability tests are carried out at constant oxygen conversion of 35%.

Example

8 g of cesium fluoride dissolved in 832 ml water was mixed with 800 g of Kaiser alumina (26405) (Al₂O₃.H₂O) by addition of the cesium fluoride solution to the alumina, and the mixture was kneaded during 30 min. The obtained paste was extruded. The obtained shaped pieces were dried at 120 °C and then calcined at periodically increased temperature. Up to 700 °C was calcined firstly at an increase in temperature of 200 °C/h, then was calcined for one hour at 700 °C, whereafter the temperature in two hours reached 1600 °C. Finally was calcined further for one hour at 1600 °C. The pore volume of the alpha-alumina shaped pieces was 0.45 ml/g and the average pore diameter was 1.6 µm. The obtained ring-shaped pieces were impregnated with an aqueous solution of silver oxalate, to which cesium hydroxide, ammonium perrhenate and ammonium sulphate was added. The impregnation was carried out for 10 min under vacuum, whereafter the shaped pieces were separated from the aqueous solution, and then placed in a heat air stream at a temperature of 250-270 °C during 10 min, in order to convert the silver oxalate into metallic silver. The aqueous solution of silver oxalate contained 28 per cent by weight of Ag (calculated on the total weight of the solution), wherein the silver oxalate was complexed with ethylene diamine and to which solution had been added cesium hydroxide, ammonium perrhenate and ammonium sulphate. The impregnated shaped pieces before heat treatment contained 17.1 per cent by weight (calculated on the weight of the total catalyst) of silver and 280 ppm of cesium per million parts and 1 micromole of ammonium perrhenate and 1 micromole of ammonium sulphate per gram of total catalyst). The pieces were subsequently calcined.

A steel cylindric reactor with a length of 15 cm and a diameter of 3 mm was filled completely with catalyst particles of about 0.3 mm. The reactor was placed in a bath, which consisted of silicium/aluminium particles in a fluidized state. A gas mixture with the following composition was conducted through the reactor: 30 mol% ethylene, 8.5 mol% oxygen, 7 mol% carbon dioxide and 54.5 mol% nitrogen and 7 parts, per million parts of gas, of vinylchloride as moderator. The GHSV was 10,000 l.l⁻¹.h⁻¹. The pressure was 15 bar and the temperature was dependent of the oxygen conversion. The measuring instruments were connected to the reactor and to a computer, in such a way that conversion and temperature could be regulated precisely. With the aid of gaschromatography or mass spectroscopy the content of each reaction component was determined. The stability test was carried out at a constant oxygen conversion of 30%. During the test, at regular intervals, the selectivity to ethylene oxide was determined. After 24 days the test was discontinued.

It was found that the selectivity of the catalyst according to the invention after 24 days had decreased 0.1 mol%, compared with its initial selectivity.

Under the same circumstances a standard catalyst showed a selectivity loss of 0.6 mol%, after already 18 days of operation.

Claims

1. A process for preparing a silver catalyst suitable for use in the oxidation of ethylene to ethylene oxide comprising impregnating an alumina carrier with a solution of a silver compound, sufficient to cause precipitation on the carrier of from 1 to 25 per cent by weight, on the total catalyst, of silver and, after precipitation, reducing the silver compound to metallic silver, characterized in that the alumina carrier is mixed with an alkali metal compound and calcined to a temperature of between 1200 °C and 1700 °C prior to impregnation with the solution of the silver compound and before, during or after that impregnation the calcined carrier is also impregnated with one or more dissolved potassium, rubidium or cesium compounds as promoter and with a rhenium compound.
2. A process according to claim 1, characterized in that a sulphur compound is also impregnated on the carrier.
3. A process according to claim 1 or 2, characterized in that the alumina carrier is mixed with cesium fluoride, cesium chloride, lithium flu-

oride, lithium nitrate or cesium hydroxide.

4. A process according to any one of claims 1-3, characterized in that an alkali metal compound is mixed with the alumina in such quantity that the atomic ratio of alkali metal/aluminium is between 0.001 and 0.1.
5. A process according to claim 4, characterized in that silicon dioxide is additionally mixed with the alumina in such quantity that the atomic ratio of silicon/aluminium is between 0.1 and 0.5.
6. A process according to any one of claims 1-5, characterized in that the enriched alumina carrier is extruded and shaped to particles, which are calcined to a temperature of between 1200 °C and 1700 °C.
7. A process according to any one of claims 1-6, characterized in that the promoter is present in an amount between 10 and 1000 parts by weight of potassium, rubidium or cesium metal per million parts by weight of total catalyst.
8. A process according to claim 7, characterized in that the promoter is present in an amount between 250 and 750 parts by weight.
9. A process according to any one of claims 1-8, characterized in that the rhenium compound is a rhenium salt or a rhenium oxide or sulphide.
10. A process according to claim 9, characterized in that the rhenium salt is a rhenate.
11. A process according to claim 10, characterized in that ammonium perrhenate is used.
12. A process according to claim 2 and any one of claims 9-11, characterized in that a sulphate is impregnated on the carrier, preferably ammonium sulphate.
13. A process according to claim 12, characterized in that the sulphate-ions are on the carrier in an amount between 20 and 500 parts by weight per million parts by weight of total catalyst.
14. A process according to any one of claims 1-13, characterized in that the amount of rhenium calculated as a metal, brought on the alumina carrier is between 100 and 2000 parts by weight per million parts by weight of total catalyst.

15. A silver catalyst, suitable for use in the oxidation of ethylene to ethylene oxide, prepared by the process of any one of the preceding claims.

16. A process for preparing ethylene oxide by oxidation of ethylene in the presence of a silver catalyst prepared by means of a process according to any one of the claims 1-14 or a silver catalyst according to claim 15.

Revendications

1. Un procédé de préparation d'un catalyseur à l'argent, utilisable dans l'oxydation de l'éthylène en oxyde d'éthylène, selon lequel on imprègne un support d'alumine avec une solution d'un composé de l'argent, en quantité suffisante pour causer une précipitation sur le support de 1 à 25 % en poids d'argent, par rapport au catalyseur total, et, après la précipitation, on réduit le composé de l'argent en argent métallique, caractérisé en ce que le support d'alumine est mélangé avec un composé de métal alcalin et calciné à une température comprise entre 1200 °C et 1700 °C avant l'imprégnation avec la solution du composé de l'argent et que, avant, pendant ou après cette imprégnation, le support calciné est imprégné aussi d'un ou plusieurs composés dissous du potassium, du rubidium ou du césium comme promoteur et d'un composé du rhénium.
2. Un procédé selon la revendication 1, caractérisé en ce qu'un composé du soufre est aussi déposé par imprégnation sur le support.
3. Un procédé selon la revendication 1 ou 2, caractérisé en ce que le support d'alumine est mélangé avec du fluorure de césium, du chlorure de césium, du fluorure de lithium, du nitrate de lithium ou de l'hydroxyde de césium.
4. Un procédé selon l'une quelconque des revendications 1-3, caractérisé en ce qu'un composé de métal alcalin est mélangé avec l'alumine en quantité telle que le rapport atomique du métal alcalin à l'aluminium soit compris entre 0,001 et 0,1.
5. Un procédé selon la revendication 4, caractérisé en ce qu'en outre du bioxyde de silicium est mélangé avec l'alumine en quantité telle que le rapport atomique du silicium à l'aluminium soit compris entre 0,1 et 0,5.
6. Un procédé selon l'une quelconque des revendications 1-5, caractérisé en ce que le support

d'alumine enrichi est extrudé et mis sous la forme de particules, qui sont calcinées à une température comprise entre 1200 °C et 1700 °C.

7. Un procédé selon l'une quelconque des revendications 1-6, caractérisé en ce que le promoteur est présent à raison d'une quantité comprise entre 10 et 1000 parties en poids de métal potassium, rubidium ou césium par million de parties en poids du catalyseur total.
8. Un procédé selon la revendication 7, caractérisé en ce que le promoteur est présent à raison d'une quantité comprise entre 250 et 750 parties en poids.
9. Un procédé selon l'une quelconque des revendications 1-8, caractérisé en ce que le composé du rhénium est un sel de rhénium ou un oxyde ou sulfure de rhénium.
10. Un procédé selon la revendication 9, caractérisé en ce que le sel de rhénium est un rhénate.
11. Un procédé selon la revendication 10, caractérisé en ce qu'on utilise du perrhénate d'ammonium.
12. Un procédé selon la revendication 2 et l'une quelconque des revendications 9-11, caractérisé en ce qu'un sulfate est déposé par imprégnation sur le support, de préférence du sulfate d'ammonium.
13. Un procédé selon la revendication 12, caractérisé en ce que les ions sulfate sont sur le support à raison d'une quantité comprise entre 20 et 500 parties en poids par million de parties du poids du catalyseur total.
14. Un procédé selon l'une quelconque des revendications 1-13, caractérisé en ce que la quantité de rhénium, calculée en métal, déposée sur le support d'alumine, est comprise entre 100 et 2000 parties en poids par million de parties en poids du catalyseur total.
15. Un catalyseur à l'argent, utilisable dans l'oxydation de l'éthylène en oxyde d'éthylène, préparé par le procédé selon l'une quelconque des revendications précédentes.
16. Un procédé pour la préparation d'oxyde d'éthylène par oxydation d'éthylène en présence d'un catalyseur à l'argent préparé au moyen d'un procédé selon l'une quelconque des revendications 1-14 ou d'un catalyseur à

l'argent selon la revendication 15.

Patentansprüche

1. Verfahren zur Herstellung eines Silberkatalysators, der geeignet ist zur Verwendung bei der Oxidation von Ethylen zu Ethylenoxid, umfassend das Imprägnieren eines Tonerdeträgers mit einer Lösung einer Silberverbindung, die ausreicht, um eine Abscheidung auf dem Träger von 1 bis 25 Gew.-%, bezogen auf den Gesamtkatalysator, an Silber hervorzurufen, und nach der Abscheidung Reduzieren der Silberverbindung zu metallischem Silber, dadurch gekennzeichnet, daß der Tonerdeträger vermischt wird mit einer Alkaliverbindung und calciniert auf eine Temperatur zwischen 1200 und 1700 °C vor dem Imprägnieren mit der Lösung der Silberverbindung, und der calcinierte Träger vor, während oder nach dem Imprägnieren zusätzlich mit einer oder mehreren gelösten Kalium-, Rubidium- oder Cäsiumverbindungen als Promotor und mit einer Rheniumverbindung imprägniert wird.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß eine Schwefelverbindung ebenfalls auf den Träger imprägniert wird.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Tonerdeträger mit Cäsiumfluorid, Cäsiumchlorid, Lithiumfluorid, Lithiumnitrat und Cäsiumhydroxid vermischt wird.
4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß eine Alkaliverbindung mit der Tonerde in einer solchen Menge vermischt wird, daß das Atomverhältnis Alkali/Aluminium zwischen 0,001 und 0,1 liegt.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß Siliciumdioxid zusätzlich mit der Tonerde in einer solchen Menge vermischt wird, daß das Atomverhältnis Silicium/Aluminium zwischen 0,1 und 0,5 liegt.
6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß der angereicherte Tonerdeträger extrudiert und zu Teilchen geformt wird, die auf eine Temperatur zwischen 1200 °C und 1700 °C calciniert werden.
7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß der Promotor in einer Menge zwischen 10 und 1000 Gew.-Teilen Kalium, Rubidium oder Cäsium pro Million Gewichtsteile des gesamten Katalysators

vorhanden ist.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß der Promotor in einer Menge zwischen 250 und 750 Gew.-Teilen vorhanden ist. 5
9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Rheniumverbindung ein Rheniumsalz oder ein Rheniumoxid oder -sulfid ist. 10
10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das Rheniumsalz ein Rhenat ist. 15
11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß Ammonium-perrhenat verwendet wird.
12. Verfahren nach Anspruch 2 und einem der Ansprüche 9 bis 11, dadurch gekennzeichnet, daß ein Sulfat auf den Träger imprägniert wird, vorzugsweise Ammonium-sulfat. 20
13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß die Sulfationen auf dem Träger in einer Menge zwischen 20 und 500 Gew.-Teilen pro Million Gewichtsteil des gesamten Katalysators vorhanden sind. 25
14. Verfahren nach einem der Ansprüche 1 bis 13, dadurch gekennzeichnet, daß die Menge an Rhenium, berechnet als Metall, die auf den Tonerdeträger aufgebracht wird, zwischen 100 und 2000 Gew.-Teilen pro Million Gewichtsteile des gesamten Katalysators liegt. 30
15. Silberkatalysator, geeignet zur Verwendung bei der Oxidation von Ethylen zu Ethylenoxid, hergestellt nach dem Verfahren nach einem der vorangehenden Ansprüche. 35
16. Verfahren zur Herstellung von Ethylenoxid durch Oxidation von Ethylen in Gegenwart eines Silberkatalysators, der hergestellt worden ist nach einem Verfahren nach einem der Ansprüche 1 bis 14 oder eines Silberkatalysators nach Anspruch 15. 40

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